

FLAVONES AND THEIR 5-GLYCOSIDES FROM
Spiraea hypericifolia

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By paper chromatography, seven substances of flavonoid nature have been found in the stems of *Spiraea hypericifolia*. In the present communication we give the results of a study of two flavones present in the plant in the free state and their 5-glycosides.

The flavonoids investigated deposited from a concentrated methanolic extract of the stems. They were separated by repeated chromatography on polyamide using as eluent solutions of methanol in chloroform with increasing concentrations of from 5 to 20 %.

Substance (1) formed faintly yellowish crystals with mp 347-348° C.

Substance (2) formed yellow crystals with mp 327-328° C, λ_{\max} 254, 351 nm.

By means of qualitative reactions, the products of alkaline cleavage, and UV spectroscopy with complex-forming and ionizing additives, substance (1) was identified as apigenin and substance (2) as luteolin.

Substance (3) formed colorless needles associated into druses which softened at 250-252° C and then reformed long fine needles with mp 294-295° C, λ_{\max} 262, 335, $[\alpha]_D^{20} - 56.2$ (c 1.08; DMFA), R_f 0.47 in system 1, 0.67 in system 2 [butan-1-ol-acetic acid-water (40:12.5:29)], and 0.19 in system 3 (15% acetic acid). The compound possessed the bright blue fluorescence in UV light that is characteristic for 5-glycosides of flavonoids [1]. Acid hydrolysis yielded apigenin and glucose, and the action of alkali gave p-hydroxybenzoic acid and phloroglucinol. The absence of shifts with $AlCl_3$ and $ZrOCl_2$ in the UV spectrum showed the attachment of the glucose to position 5 of apigenin. According to a polarimetric analysis the glycoside is a β -D-glucopyranoside, as was confirmed by the presence in the IR spectrum of three absorption bands (1050, 1065, 1085 cm^{-1}) and hydrolysis with emulsin. Thus, the flavonoid investigated is apigenin 5- β -D-glucopyranoside. A hexaacetyl derivative was obtained with mp 193-194° C, $[\alpha]_D^{20} - 49.4$ (c 1.8; chloroform), the NMR spectrum of which corresponded to the proposed structure. The constants of the substance itself and of its acetate were similar to the constants of synthetic samples obtained previously [2] and different from the constants given by other workers [3].

Substance (4) formed yellowish needles with mp 185-186° C and 280-282° C, λ_{\max} 255, 266, 352, $[\alpha]_D^{20} - 26.0$ (c 0.57; DMFA).

According to the results of acid and enzymatic hydrolysis and NMR spectroscopy, the compound under investigation was luteolin 5- β -D-glucopyranoside. Luteolin 5-glucoside has been found previously only in *Galega officinalis* [4] and *Dahlia* [5].

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